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NRL Report 5712

STUDIES OF THE MUSTARD GAS - PAINT SYSTEM

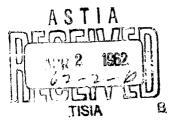
PART 1 - THE EVAPORATION OF MUSTARD GAS FROM PAINT FILMS

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February 28, 1962





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ABSTRACT

Wind-tunnel studies have been conducted to determine the evaporation kinetics of liquid drops of mustard gas (HD) from painted and nonpainted surfaces. The evaporation process has been divided into two characteristic periods: The first, the exposed-liquid-surface period, is the period in which liquid HD is exposed to the atmosphere. The second, the sorbed-liquid period, is that in which all of the remaining HD resides within the absorbent paint film.

Recognition of the two characteristic periods has led to a modified approach to evaporation theory. This approach embodies the concept of a "standard dry line." The dry line is obtained by plotting t/P_e against t at various experimental conditions, where t is the evaporation time, and P_e is the percent of HD evaporated at that time. When evaporation is complete, i.e., P_e = 100%, the terminal points, for the different conditions, are found to form a straight line, i.e., the dry line. One consequence of the standard dry line concept is a method for determining or evaluating the sorbing power coefficient (K_{sp}) of paint films. The sorbing power of paint films is the ability to absorb HD under a given set of experimental conditions. The K_{sp} values of paint films in these studies range from 0.08 to 0.77. A small value is desirable from the decontamination viewpoint.

There were no apparent differences in the behavior for the various types of paints used.

PROBLEM STATUS

This is an interim report; work on the problem is continuing.

AUTHORIZATION

NRL Problem C08-22
Projects SF 011-08-01, Tasks 3330, 3331
3332, 3334, 3335, 3336; SF 011-08-09, Tasks 1730
1726; and SF 011-08-02, Task 0508

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STUDIES OF THE MUSTARD GAS - PAINT SYSTEM

PART 1 - THE EVAPORATION OF MUSTARD GAS FROM PAINT FILMS

INTRODUCTION

One of the technological problems involved in effective battle control of the U.S. Fleet is the decontamination of naval ships and installations after chemical warfare (CW) attack (1,2). Decontamination, the process of destroying, removing, or neutralizing CW agents or their effects, can be done by chemical action, physical removal, sealing, heat, steam, and weathering (1,2).

Most of the CW decontamination methods have been and are being studied by the Army and Navy. However, little quantitative information is available on the effects of weathering. Decontamination by weathering relies on the effects of the rain, sun, and wind to alter and/or remove CW agents.

Weathering is one of the simplest means of decontamination. For reliable and effective use its inherent limitations must be known and understood. For example, strong sunlight promotes evaporation; rain, spray, or dew hydrolyzes some CW agents and serves as a natural washdown system; and the wind promotes evaporation of all CW agents.

In some cases, particularly after the surface removal of CW deposits by chemical action,* washdown, evaporation, or steam, the only available means for dealing with CW residues in paintwork or other absorbent surfaces is weathering. Granted sufficient time, weathering will decontaminate any area exposed to the atmosphere, even heavily contaminated areas.

To determine the effects of these factors on the evaporation rates of liquid toxic agents, mustard gas (HD) (3-6) was chosen as a typical CW agent for experimental purposes. The reasons for this choice were: (a) it is easier to work with in the laboratory than some of the more toxic agents, and (b) the evaporative behavior of the more toxic agents should differ from HD in a systematic way, i.e., via the physical properties.

THE EVAPORATION PERIODS AND THE CONCEPT OF THE STANDARD DRY LINE

General Procedure

Freshly painted, well-aged painted, and unpainted metal panels were preconditioned in a wind tunnel at the desired air temperature prior to contamination with HD. The preconditioning was necessary to establish temperature equilibrium between the material to be contaminated and the HD and to allow the loss of volatile constituents to assume a steady rate from the paint film. The preconditioning usually took about 48 hours.

^{*}It is not widely recognized that chemical decontaminants such as DANC and DS2 are not capable of neutralizing CW agents absorbed in paint unless they destroy the paint film as well. However, the time element is a major factor in all aspects of Fleet operations. It is therefore vital to evaluate the influence of all factors controlling the weathering of CW agents. These factors are: wind speed, surface temperature, the CW agent or agents involved, and the composition and thickness of the paint film.

The test panels were removed from the wind tunnel, weighed to the nearest tenth of a milligram, contaminated with liquid drops of HD, reweighed, and placed back in the wind tunnel immediately. At periodic intervals the contaminated panels were analyzed for residual HD after evaporation. The analysis was carried out either gravimetrically or chemically (6). At the same time, blanks, i.e., noncontaminated painted panels, were also analyzed. This was done to correct the loss of any volatile constituents from the paint films not accounted for by the preconditioning.

Equipment and Material

<u>Wind Tunnel</u> - A wind tunnel in an air-conditioned, stainless-steel-lined room was used to determine the rates of evaporation and other related phenomena of liquid toxic agents (Figs. 1(a), 1(b), 1(c)). This wind tunnel has a 0.5-sq ft cross-sectional area and is powered by a positive acting 2-hp electric motor blower unit which forces laboratory air through the tunnel. The room was maintained at a slightly lower pressure (about 0.5 inch of water) than the surrounding laboratory area in order to prevent toxic agents from escaping into the main laboratory, a procedure especially important when handling CW agents more toxic than HD. In addition, a carbon adsorbing bed was inserted in the wind tunnel to remove toxic vapors emanating from the working section of the tunnel.

The exhaust air from the stainless steel room and that coming through the carbon bed are transferred by ductwork to the laboratory roof. There, the air passes through a special filter apparatus containing a particulate filter and carbon bed before being discharged into the atmosphere.

Metal screens are inserted between the blower and the working section of the wind tunnel to regulate the wind speed; the screens create a laminar flow of air parallel to the contaminated paint surface samples. Following the screens are located a section of expanded metal lath to afford a controlled degree of turbulence in the working section.



Fig. 1(a) - The mouth of the wind tunnel. The attached blower was used to produce the higher wind speeds of 0.9, 6.1, and 16.1 mph. The Flowrator on top of the wind tunnel was used to measure the air bled from the laboratory compressed air line for 0.1 mph.

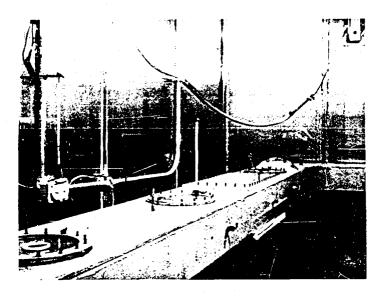


Fig. 1(b) - The working section of the wind tunnel. It has a cross-sectional area of 0.5 sq ft. The top and bottom consist of quarter-inch transparent sheeting so that the evaporation behavior of the HD can be observed.

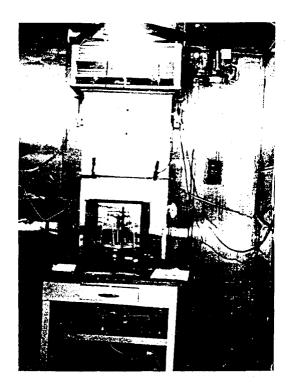


Fig. 1(c) - The analytical balance and the carbon bed directly behind it

The air temperatures in the wind tunnel and in the stainless-steel-lined room are controlled by heating elements within the room. The temperatures investigated were 30° , 40° , and 50° C, each controlled to $\pm 1.0^{\circ}$ C.

Test Panels - The test panels, painted and unpainted metal (tin plate 2.5 inches square, were contaminated with HD by means of a multi-pronged tool known as a dipper (Fig. 2). The dipper consisting of 76 prongs (nails with heads and points cut off), was constructed at this Laboratory for the purpose of contaminating surfaces with liquid drops of CW agents in a reasonably reproducible manner.



Fig. 2 - The dipper, test panels, and the HD reservoir

The dipper is immersed into a metal pan which contains a standard depth of HD. After a few seconds the dipper is removed from the metal pan and pressed lightly against the paint surface for a few seconds. Experience with this technique allows the transfer of uniform drops of HD to the test panels. The total paint area wetted by this method is approximately four sq cm.

Paint Films - The paint films investigated were of two kinds, typical of those usually used aboard ship. Pertinent information on the paints used is given in Table 1.

The thickness of paint films varied from two to sixteen mils. The values of the paint thickness given in the experimental data are average values determined by taking the mean of several micrometer measurements. The ages of the paint films studied were freshpainted films (two weeks to one month old) and well-aged paint films (eight years old and laboratory weathered). All the painted samples were aged in the laboratory and were not exposed to outdoor conditions.

Discussion

Basic Process - Table 2 gives the results of the evaporation of HD from metal (tin plate) surfaces at various experimental conditions and Table 3 gives the results of the evaporation of HD from painted surfaces under similar conditions. If the experimental data of Tables 2 and 3 were plotted linearly, a general type evaporation-time curve (Fig. 3), which describes an evaporative process would be obtained. The evaporation process of liquids and drying of solids in general has been and is being studied by many investigators (7-13). However, since the type of evaporation process of interest in this discussion is somewhat at variance with the type of drying usually considered, a different approach has been used. A close analogy, however, exists between the usual drying theory and the one given in this report.

The initial condition in the modified approach is that the paint film surface and interior be HD-free. The paint surface is then contaminated with HD in the form of liquid drops. Liquid drops are used because militarily it would be the most probable way in which a surface could be contaminated.

Table 1 Composition of Naval Paints

Mil-Spec-P-15130A	Mil-Spec-Jan-P-699
Light gray haze	Dark gray haze
Type formula 5H	Type formula 20A
Deck paint	Superstructure paint
Chemical composition: TiO ₂	Chemical composition: TiO ₂
ZnO	ZnO
Lampblack	Lampblack
Mg silicate	Mg silicate
-	Silica (pulverized)
Alkyd resin	Alkyd resin
-	Phenolic resin
Petroleum spirits	Petroleum spirits
Pb naphthenate	Pb naphthenate
Co naphthenate	Co naphthenate
Mn naphthenate	Mn naphthenate

Table 2
Wind Tunnel Evaporation of HD from a Metal Surface

Commis	Original	Wind		Time for Complete					Evap	orate	HD (%)			-	
Sample No.	Wt. of HD (g)	Speed (mph)	(°C)	Evap. (min)	15 min	30 min	45 min	60 min	90 min	120 min	150 min	180 min	240 min	300 min	360 min	420 min
1	0.0530	0.1	30	465	_	-	-	15.7	-	33.4	-	47.0	63.8	78.5	91.1	96.0
2	0.0471	0.1	30	345	-	-	-	23.4	-	44.6	-	63.1	83.2	96.1	-	-
3	0.0387	0.1	40	165	-	25.0	-	52.0	73.5	96.0	98.5	-	-	-	-	-
4	0.0530	0.1	40	225	-	20.0	-	41.0	56.0	72.0	83.5	96.0	-	-	- 1	-
5	0.0484	0.1	50	96	16	30	46	63	95	-	-	-	-	-	-	-
6	0.0413	0.1	50	87	17	33	51	68	-	-	-	-	-	-	-	-

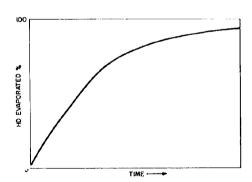


Fig. 3 - General evaporation-time curve

Table 3 Wind Tunnel Evaporation of HD from Paint Films

				:	[:								•	:		!	1	1	!			į			ļ		Γ
			Original Wr of HD	Wind	Paint											Evaj	orate	Evaporated HD (%)	£0									-
Temp. and Age of Paint	Sample Paint No. Type	Paint Type	Surfa	Speed (mph)	Thickness (mils)	(min)	c nin	5 m	15 min	20 Z	25 3 min m	30 40 min min	40 50 min min		66 99 mim mim	120 min	150 min	180 min	240 3 min n	300 ri ii	330 3 min	360 4 min r	420 4 min	480 15 min	1360 13 min m	1380 1440 min min		2880 min
			(8)		ά .	233		: -	,	i	<u> </u>	1. 1		24.0	10	48.2	-	70.4	85.0 87.0	7.0	- '	89.2	-		Ė	. 62		99.1
30, C	~ 0	AUA	0.033		0.6	02	,					'		50.5	1	70.0	,	80.5	87.0 93.1	3.1				6.59	<u>.</u> -	6	95.0	99.4
8-Year-Old			0.040.0		0 6	20	•		•					88.1		91.8	•	92.3	,		, ,	94.2	,		_		_	
Paint	n -	U 00	0.0302	1. 9.	2.0	22				•	-8	84.3	•	97.1		,	,	-	96.6	97.5		-	-	,		'		
	2	F03					:	1	+ -			-	'	25.0	<u></u>	49.0	ļ-,	74.9	76.8		-8	86.1				8	96.8	99.0
40°C -	11	Э.	0.0410	0.1	3.0	6	1							9		4 4	,		94.7						<u>.</u>	%	99.2	
8-Year-Old	12	20A	0.0396	6.0	0.7	2	,	•						9 8			- (99.5				<u>'</u>		_	
Paint	13	ЭН	0.0365	6.1		8 %				• •	6	92.6		96.3		0.06		97.76	99.5		-				- <u>-</u> -			-
	14	2Н	0.0753	16.1	3.0	g	.		1	+	-		+		1				+	+	-	6	-	+		<u>'</u>		-
50°C -	15	2H	0.0490	0.1	5.1	82	٠	•			÷			•	٠.	81.6	,		6.88		,,	9. 1.						
8-Vear-Old	91	20A	0.0604	6.0	2.0	8		41.4		72.5	80	7.7 88	87.7 88.9 91.4	4 92.1	•	95.4	•	<u>. </u>	6.96							' 		
Dei-t	1 1	406	0.0586	9	3.0	52		51.9	 -	85.3	<u></u>	90.8 92.2	.2		•	95.4	•	•	97.3		,							
ramii.		Ç #		16.1	3.0	2	•	82.5		89.5	6	91.6	1	95.2	,	87.8	•		99.4				-		-		<u> </u>	.]
	3	3							1		-	'	-	Ŀ	30.1	35.6		48.0	59.5 68	68.6	- 1	73.1	_	· ·	<u>.</u>	8	90.5	94.2
30°C -	19	20A	0.0242	0.1	5.0	27.3		•	•			-		44			-		_ _	0.16					<u>.</u>	- S	9.96	99.3
Fresh Paint	8	2H	0.0411	6.0	2.0	8				 1	· 		-	; ;		. 5			_					_	<u> </u>	<u>.</u>	<u>.</u>	
	17	2H	0.0384	6.1	3.0	35			•		· •				•	0.78					,	9				<u>.</u>		
	22	20A	0.0579	16.1	0.9	22	ı		•	•			•	<u>.</u>		•		-	- 1			3	+	+	+	+	+	-
0,01	ş	i i	0.0357	[]	5.0			,					•	1		58.0	ı	-	82.0		87.0		 I			6	92.2	
· · · · · · · · · · · · · · · · · · ·	3 2	5	0.000	0	<u>.</u>	45		•	,		<u>.</u>		_	82.0		0.06	,	,	ا	27.7	 F	_			_	5	97.3	
Fresh Faint	5 8	¥ ;	2,470	; ;			,				86	83.0 -		89.1	1	1	91.5	,	94.4 96.0	5.0	-						<u> </u>	
	3 8	H.	0.0749	16.1	0.9	25	•		,				<u> </u>	85.0	•	-			,		,	28.7			+			. T
	1		10.00	;		ç	'	100	Ī.	22.5	1	31.5 38	38.0 43.5	5 48.2		69.5	,	77.0	•			•		-	<u> </u>		87.2	
- ၁ ၁	7 6	F .	0.0323	-	9 6	3 %	=	2 0	3	11 0 21 0 31 0 42.0 47.0		_'.	_	78.9	•	87.1	,	•	-	_		 I		·	87.5			
Fresh Paint	8 8 ——	# E	0.000.0	, 4	6. 41	3 8	17.0	34.0	46.0	56.0		•	-	73.5	,	80.7	٠,		•	_	,	•		о 	91.1			
	8 8	g #	0.010	16.1	14.0	: 2		57.3			-	71.0 73.2	.2 74.9	9 77.8	ı	81.4		83.5	•			•	-	-				
	3 1	3 3		:	c	6		,	Γ.	Ϊ,	+ :		 '	21.3	,	35.0	,	51.5	86	89.3		,	89.7		1	- i	95.1	
30,C-		표 	0.0310	:		3	,							17.3	,	ă,	,	5 04	<u>~</u>	76.2		79.7 87.0	37.0	,	_	8	8.96	
8-Year-Old	35	2Н	0.0370		7.5	98 :		1					- 1	11.0	,	22.5	-	35.5		62.4	,	74.9	80.0				87.0	88.2
	1	E	0.0458	1.5	13.0	į	╧			\dagger	+	+	+					Ť	0 0 0 0 0	١,	١,	7 2			ъ Б	90.4	- 6	95.1
30°C-	35	20A	0.0344	0.1	9.0	247	•			,			-	1		27.0			0 0	, ,		. 4		,	7	. 8.92	· ·	83.0
Fresh Paint	32	20A	0.0371	0.1	8.0	125	•			1		<u>. </u>	_	•		25.8		1	41.849.0		- 4				. 19	9.	<u>ت</u> ق	6.69
	36	20A	0.0422	0.1	13.0	119	•	•	•	,	-	-	-	-	1	23.5	-	•	32.9 38.9					-			1	
	1			1	on the fire	,																						

*Time at which the paint surface becomes visually HD-free.

ı

Evaporation of HD from a Metal Surface – The evaporation of HD from metal surfaces is given in Table 2. These data can be recalculated and arranged as shown in Table 4, where t is the evaporation time in minutes and P_e is the percent of HD evaporated at time t.

When the data from Table 4 are plotted, a series of curves are obtained as shown in Fig. 4. The advantages of this plot as a means of organizing the data for studying the free-liquid evaporation phase will be seen in the discussion following.

			Ta	ble 4		
t/P	Values	of	HD	from	Metal	Surfaces

	Original	m								t/P _e					
Sample		Temp. (°C)	15 min	30 min	45 miņ	60 min	90 min	120 min	150 min	180 min	240 min	300 min	360 min	420 min	At complete evap.
1	0.0530	30	-	-	-	3.8	-	3.6	-	3.8	3.8	3.8	4.0	4.4	4.7
2	0.0471	30	-	-	-	2.7	-	2.7	-	2.9	2.9	3.1	-	-	3.5
3	0.0387	40	- 1	1.2	-	1.2	1.2	1.3	1.5	-	-	-	-	-	1.7
4	0.0530	40	-	1.5	-	1.5	1.6	1.7	1.8	1.9	-	-	-	-	2.3
5	0.0484	50	0.9	1.0	1.0	1.0	1.0	-	-	-	-	-	-	-	1.0
6	0.0413	50	0.9	0.9	0.9	0.9	-	-	-	-	-	ļ -	-	-	0.9

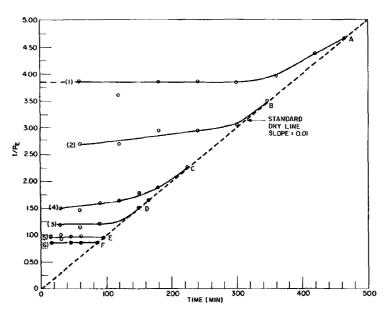


Fig. 4 - Plotting of "standard dry line" from data of Table 4

In Fig. 4 points A, B, C, D, E, and F signify that evaporation is complete, i.e., the metal surface is liquid-free. If these terminal points are connected, a line results which, when extrapolated, passes through the origin. This line will hereafter be designated as the "standard dry line." Since P_e at complete evaporation is 100%, the slope of the "standard dry line" is 0.01. This will apply to any and all experimental conditions. Therefore, under a given set of experimental conditions the evaporation curve will terminate at the "standard dry line" when the process is complete, i.e., at complete evaporation the contaminated system will be HD-free, or dry.

Inspection of Fig. 4 and visual observation of the drop-evaporation process indicates that the evaporation of HD from metal surfaces occurs as follows: As the liquid drops of HD make contact with the metal surface, they spread over the surface until a final advancing contact angle is made (14,15). This usually occurs within a few seconds. From this time on, evaporation proceeds at a constant rate. This is shown in Fig. 4 by the flat section of the curves. Finally, as the originally contaminated area decreases, i.e., the drop "dries up," the rate of evaporation appears to decrease. The rate of evaporation (mass evaporated per unit area per unit time, e.g., g/cm^2 -sec) appears to decrease because under these experimental conditions the proper correction for the actual area of liquid surface cannot be made. Furthermore, as evaporation of the liquid drops proceeds, they become smaller and the contaminants originally present (HD used here was 99.5% pure) begin to exert their influence to a significant extent. Consequently, the rate of evaporation at the end will decrease. This is shown in Fig. 4 by the knee of the curves A, B, C, and D.

The factors that influence the observed evaporation rate are (a) the temperature of the system, and (b) the wind speed flowing parallel to the contaminated surface.

Evaporation of HD from Paint Films - Initially, or soon after contact of HD with a paint film, the following phenomena occur: (a) wetting of the paint film surface, (b) penetration into the paint film interior, and (c) evaporation into the atmosphere. For the present discussion the wetting and spreading of HD on paint surfaces will be omitted. This work is continuing and will be reported at a later date. The omission of this information will in no way detract from the present discussion.

Evaporation and penetration occur until at some finite time the paint surface becomes visually liquid-free. This means that an effective zero concentration of HD exists at the paint surface at that time. For purposes of this study, the paint surface includes the laminar sub-layer. The time at which the paint surface becomes visually HD-free has been designated as $t_{\rm LFS}$. After time $t_{\rm LFS}$ the sorbed HD within the paint film diffuses back to the paint surface, and, hence, out into the atmosphere. This process continues until evaporation is complete.

It might be worthwhile to mention here that saturation of the paint film with HD rarely, if ever, occurs under the above conditions. Consequently, when the paint surface becomes visually HD-free the concentration density of HD within the paint film does not approach saturation. On the other hand, thin paint films should show a higher concentration density than thicker paint films.

Given in Table 5 are the t/P_e values tabulated from the experimental evaporation data of Table 3. A few representative samples are shown in graphical form in Figs. 5-10. It should be noted that some of the curves converge to the standard dry line as expected while others are parallel to and even diverge from the dry line.

It is instructive to show a general evaporation curve as an aid in describing the evaporation process of HD from painted surfaces (Fig. 11).

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Table 5

							P. Va	alues o	of HD	from :	Paint !	Films							
Test										t/Pe									
Sample	5 min	10 min	15 min	20 min	25 min	30 min	40 min	50 min	60 min	90 min	120 min	180 min	240 min	300 min	360 min	420 min	480 min	1440 min	2880 min
7		-	-		-	-	•	-	2.50	-	2.49	2.56	2.82	3.45	4.04	-	-	15.1	29.1
8		-	-	-	-	-	-	-	1.19	-	1.71	2.24	2.76	3.22	- !	-	5.01	14.8	29.0
9		-	-	-	-	-	-	-	0.68	-	1.31	1.95	-	~	3.82	-	-		-
10		- '	- 1	-	-	0.36	-	-	0.62	- 1	-	-	2.48	3.08	-	-	-	-	-
11		-	-	-	-	-	-	-	2.40	-	2.45	2.40	3.12	-	4.18	-	-	14.9	29.1
12		-	-	-	-	-	-	-	0.75	-	1.27	-	2.53	-	-	-	-	14.5	-
13		-	-	-	-	0.32	-	-	0.62	-	1.22								
14		-	-	-	-	0.33	-	-	0.62	-	-	1.84	2.41						
15		-	- '	-	-	0.3	-	-	-	-	1.47		2.67		3.92			'	
16		0.24	-	0.28	-	0.34	0.45	0.55	0.65		1.26		2.49						
17	ļ	0.19		0.23		0.33	0.43		}		1.26		2.47				!		
18		0.14		0.23		0.33			0.66		1.27		2.53						Ì
19									ļ	2.99	3.38	3.75	4.04	5.12	4.92			15.9	30.6
20]		1.35		ļ	2.08		3.30	1		İ	14.9	29.0
21			•				<u> </u>		0.75		1.38		2.55						
22		0.24		0.31		0.41	0.51						2.57		3.75		1		
23	[2.07		2.93		ĺ			15.6	
24									0.73		1.33			3.17				14.8	!
25			!			0.36			0.67			1.98	2.54	3.13		ļ			
26		0.25		0.30		0.38		ļ	0.71						3.65				
27		0.83		0.89		0.95	1.05	1.15	1.24		1.73	2.34		!			1	16.5	
28	0.45	0.48	0.48	0.48	0.53				0.76	1	1.38				4.11				
29	0.30	0.30	0.33	0.35					0.82		1.49		1	ļ	3.95			i	
30		0.17		0.30]	0.41	0.55	0.67	0.77		1.47	1]		ļ		
31	İ		1		!				2.81		3.43	3.50		3.36	1	3.57		15.2	29.5
32		i i					1		3.47		4.21	4.44		3.94	4.52	4.83		14.9	
33	1								5.5		5.3	5.1		4.81	4.81	5.26		16.5	32.7
34									İ	1	4.44	Ì	4.92	1	5.45			15.3	30.3
35											4.65		5.74		6.55			18.0	34.7
36		<u> </u>	1.				İ	l		<u> </u>	5.11		7.29	7,71	8.63		1	32.9	41.1

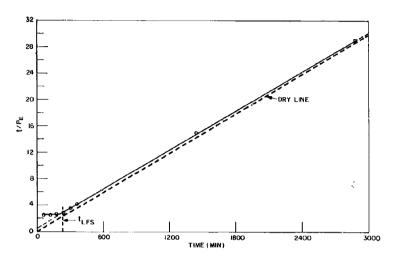


Fig. 5 - Plot of t/P_e vs time, sample 7

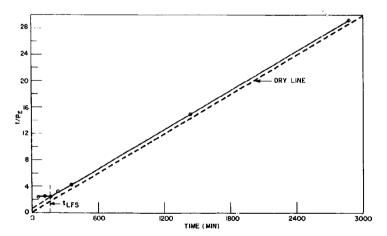


Fig. 6 - Plot of t/P_{\bullet} vs time, sample 11

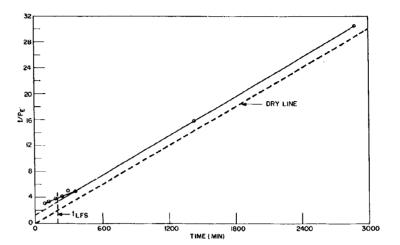


Fig. 7 - Plot of t/P_e vs time, sample 19

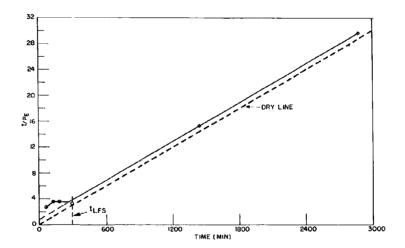


Fig. 8 - Plot of t/P_e vs time, sample 31

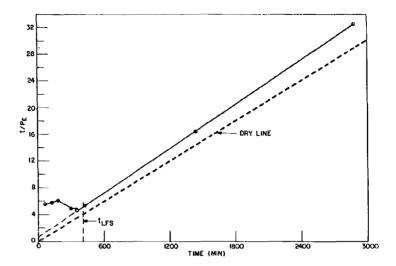


Fig. 9 - Plot of t/P_e vs time, sample 33

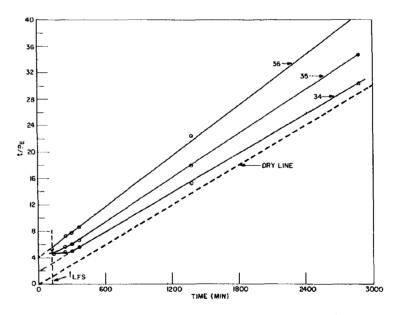


Fig. 10 - Plot of t/P_e vs time, samples 34, 35, 36

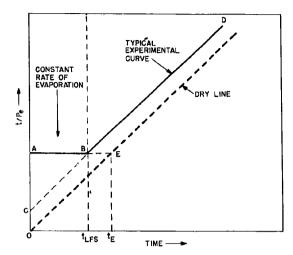


Fig. 11 - General evaporation curve of HD from painted surfaces

The evaporation process can be divided into two periods if a dotted line is drawn through $t_{\rm LFS}$ (point B) in Fig. 11. The first period is the one in which liquid HD is on the paint surface and remains exposed to the atmosphere. This will be designated as the exposed-liquid period (curve AB). After the paint surface is free of liquid HD, the region to the right of the vertical $t_{\rm LFS}$ line ensues. This region is identified with HD that remains within the paint film and will be designated as the sorbed-liquid period (Curve BD). Therefore, the evaporation process is divided into exposed-liquid and sorbed-liquid periods. The principal justification for this division rests in the experimental data. However, further justification for such division follows from the close relationship to practical shipboard decontamination procedure. One class of decontamination procedure on board ship is concerned with the removal of CW agents from the paint surface by washdown or hosing. The other procedure is concerned with the decontamination of the paint-film interior by evaporation or steaming.

The factors that affect the observed rate of evaporation of HD in the exposed-liquid period are the temperature of the system and the wind speed flowing parallel to the contaminated paint surface. These factors are identical with those from the evaporation of HD from a bare metal surface.

The factors that affect the observed rate of evaporation of HD in the sorbed-liquid period are (a) the temperature of the system, (b) the area of the paint surface initially contaminated with HD, (c) the paint film age, (d) the paint film thickness, (e) the composition of the paint film, and (f) wind speed. The wind speed is of secondary importance in that its function is to maintain an effective zero concentration of HD at the paint surface. This allows a concentration difference to occur between the paint film interior and the paint surface. In effect, a driving force is created due to the concentration difference. This allows the diffusion of the HD, within the paint, to the paint surface and out into the atmosphere.

Analysis of the evaporation process indicates that even when apparently dry portions of the originally wetted paint area appear, the evaporation rate is still constant until point B is reached. This is especially true with thin paint films. The implication here is that the sorbed HD in the apparently dry portions furnishes enough HD to the paint surface to

maintain a constant diffusion rate until finally the surface becomes truly liquid-free. For thicker paint films, sufficient HD is not furnished to the paint surface to maintain a constant rate to t_{LES} .

After $t_{\rm LFS}$ has been reached, as shown by point B in Fig. 11, the evaporation rate continually decreases. This is shown by line BD. Theoretically, when evaporation is complete, line BD must terminate at the dry line. The time when this occurs is relatively long.

Line BD should converge to the dry line in an asymptotic manner. This is the observed behavior for thin paint films (Fig. 5). However, for thicker paint films the curve actually diverges from the dry line (Fig. 10). The reason for this singular behavior is believed to be due to the distribution of the concentration density (g/cm^3) of the HD within the paint film. For thin paint films the time that liquid HD is present on the paint surface is sufficient for a uniform distribution of the HD to occur within the paint film. Unpublished data show that a 3-mil, 58-day-old paint film is penetrated by liquid HD in a few minutes. This time is short compared to the $t_{\rm LFS}$ observed here. This allows a normal diffusion of the HD from the impermeable metal/paint interface to the paint/air interface. Since diffusion of the HD is in one direction, i.e., toward the paint/air interface, the BD line in Fig. 11 will approach the dry line asymptotically.

In the thick paint films, t_{LFS} usually occurs before uniform distribution of HD is reached. One of the reasons for this is because approximately the same amount of HD was used to contaminate the surface of the thick paint films as was used for the thin paint films. Tests indicate that 14-mil, 58-day-old paint film is penetrated by liquid HD in about 150 minutes. Consequently, there was not sufficient time in all cases for uniform distribution of HD.

For uniform distribution of HD to occur within these thick paint films, a long period of time is required after t_{LFS} . In this long period, diffusional flow of HD within the paint film is not only toward the paint surface but also toward other regions of lower HD concentration, which is away from the surface. When this occurs, line BD in Fig. 11 diverges quite prominently from the dry line as shown in Fig. 10 (samples 35 and 36).

After a uniform distribution of HD within the paint film finally occurs, diffusional flow will be toward the paint surface. From then on the BD line in Fig. 11 will converge toward the dry line. This is not shown in the graphs (Figs. 9 and 10) because experimental data are not available at the long periods of time necessary for convergence. This behavior will be considerably clarified in a later report on the determination of the diffusion coefficients of HD into and out of paint films.

The important point in this discussion from the decontamination point of view is the desirability of decreasing the amount of HD sorbed into paint films. Data presented in this report show that aged paint films, due to oxidation and/or polymerization during daily exposure to the atmosphere, sorb less HD than fresh paint films. This implies that during wartime conditions the normal desires for a clean, freshly painted ship be minimized insofar as the exposed painted surfaces are concerned. In addition, any barrier at the paint surface, such as dirt, grease, or water, will tend to decrease the amount of HD sorbed by the paint.

Finally, there does not appear to be any predictable difference in behavior of the two kinds of paint studied in this report. Any differences, if real, would be due to the composition of the paint films.

THE SORBING POWER COEFFICIENT OF PAINT FILMS TO MUSTARD GAS

Introduction

Paint films are of such a complex nature that they can rarely be well-defined. Factors such as (a) film thickness, (b) age, (c) composition, (d) loss of volatile constituents during aging, and (e) the physical nature of the paint surface, contribute to the complexity of paint films in HD sorption. Some generalization, or parameter, that would be common to all paint films is needed. At the same time the generalization should enable one to obtain information pertaining to the overall picture of the evaporation of liquid CW agents from paint films.

Such possibility exists when one considers that paint films are permeable materials. This means that paint films will sorb liquids to an extent depending on the properties of the liquid, the paint film, and the evaporation conditions.

Discussion

After a paint surface is contaminated with HD, the paint surface will become visually HD-free at some finite time $\,^{\rm t}_{\rm LFS}.\,^{\rm t}$ Assume that a paint surface was impermeable to HD. Assume further that complete evaporation occurred at $\,^{\rm t}_{\rm E}.\,^{\rm t}$ This is indicated on the dry line at point E (Fig. 11). This implies that no penetration of HD into the paint film occurred and is identical to the evaporation of HD from a metal surface. Consequently, the sorbing power of a metal surface or an impermeable paint surface is zero. Inspection of Fig. 11 shows that BE is proportional to the amount of HD sorbed by the paint film and that ABE is proportional to the total amount of HD. Therefore, BE/ABE is the fraction of HD sorbed by the paint film and is hereby defined as the sorbing power coefficient $\,^{\rm t}_{\rm sp}$.

$$K_{\rm sp} = \frac{\rm BE}{\rm ABE} . \tag{1}$$

From Fig. 11 it is seen that Eq. (1) can also be written as

$$K_{sp} = \frac{t_E - t_{LFS}}{t_E}, \qquad (2)$$

where t_E is the time an impermeable surface becomes liquid-free. Hence, a ready method exists for the quantitative determination of K_{sp} . The values of K_{sp} depend on the physical properties of HD and the paint, and also on the evaporating conditions (temperature and wind speed). It is a dimensionless quantity ranging from zero to unity. Impermeable surfaces such as base metal will have K_{sp} of zero. Paint films, on the other hand, will have values of K_{sp} greater than zero but less than unity. Values of K_{sp} calculated from Eq. (2), are listed in Table 5.

Due to the ill-defined nature of the paint films, only general trends can be deduced from Table 6. For well-aged paint films, such as the eight-year-old samples, Table 6 shows that $K_{\rm sp}$ is not significantly altered by changes in temperature, wind speed, and paint film thickness. Moreover, there is no significant difference between the 5H and 20A paints. The average $K_{\rm sp}$ value for the eight-year-old-samples is 0.20.

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Table 6
Sorbing Power Coefficient of Paint Films With Respect to HD

Sample	Paint Type	Paint Age	Temp. (t°C)	Wind Speed (mph)	Paint Film Thickness (mils)	K _{sp}
7	20A	8-yr-old	30	0.1	2.8	0.15
8	5H	8-yr-old	30	0.9	3.0	0.21
9	5H	8-yr-old	30	6.1	3.0	0.13
10	20 A	8-yr-old	30	16.1	2.0	80.0
11	5H	8-yr-old	40	0.1	3.0	0.35
12	20 A	8-yr-old	40	0.9	4.0	0.13
13	5H	8-yr-old	40	6.1	3.1	0.13
14	5H	8-yr-old	40	16.1	3.0	0.13
15	5H	8-yr-old	50	0.1	5.1	0.23
16	20 A	8-yr-old	50	0.9	5.0	0.17
17	20 A	8-yr-old	50	6.1	3.0	0.17
18	5H	8-yr-old	50	16.1	3.0	0.23
19	20 A	Fresh	30	0.1	5.0	0.33
20	5H	Fresh	30	0.9	5.0	0.23
21	5H	Fresh	30	6.1	3.0	0.21
22	20 A	Fresh	30	16.1	6.0	0.39
24	20 A	Fresh	40	0.9	5.0	0.61
26	5H	Fresh	40	16.1	6.0	0.32
27	5H	Fresh	50	0.1	5.0	0.63
28	5H	Fresh	50	0.9	5.0	0.50
2 9	5H	Fresh	50	6.1	14.0	0.49
30	5H	Fresh	50	16.1	14.0	0.41
31	5H	8-yr-old	30	0.1	2.7	0.21
32	5H	8-yr-old	30	0.1	5.1	0.21
33	5H	8-yr-old	30	0.1	13.6	0.17
34	20A	Fresh	30	0.1	5.0	0.49
35	20A	Fresh	30	0.1	8.0	0.53
36	20A	Fresh	30	0.1	13.0	0.77

For the fresh-painted films, general trends are more obvious. At 40° and 50°C, an increase in wind speed decreases $K_{\rm sp}$. At the same temperature and wind speed, $K_{\rm sp}$ increases with increase in paint film thickness (samples 19-22; 34-36). At the same wind speed and paint thickness $K_{\rm sp}$ tends to increase with increase in temperature.

Values of K_{sp} for various painted surfaces can be determined aboard ships. This would be done by placing a small drop of HD on the painted surface and the same size drop of HD on an adjacent bare metal surface. It is assumed that the contact angles are the same on both surfaces. The times that these two surfaces become liquid-free can be determined visually. Therefore, a sorbing power coefficient can be deduced from an equation similar to Eq. (2), i.e.,

$$K_{sp} = \frac{t_m - t_p}{t_m} \tag{3}$$

where t_m is the time in minutes the metal surface becomes liquid-free, t_p is the time in minutes the painted surface becomes liquid-free, and K_{sp} is the sorbing power coefficient. K_{sp} in Eq. (3) may be slightly different from the K_{sp} obtained from Eq. (2). The reason for this difference is due to the method of determining the values. For practical purposes, it is believed that the two values may be considered identical. At the present time a non-toxic simulant for HD for this purpose is not known, but a search for such a substance is in progress.

Conclusions

The concept of the "standard dry line" has been used in describing the evaporation process. This has been deduced from the evaporation of mustard gas from metal surfaces. The experimental data are plotted as t/P_e against t, where P_e is the percent of HD evaporated at time t in minutes, for various evaporation conditions. When evaporation is complete from metal surfaces it is found that the final t/P_e values can be connected with a straight line passing through the origin.

From the concept of the standard dry line a sorbing power coefficient for a given sorbent can be obtained. This is the ease with which a given paint film absorbs mustard gas under given evaporation conditions. It is defined as the time a metal surface becomes liquid-free (t_E) minus the time a painted surface becomes liquid-free, (t_{LFS}) divided by (t_E) . Its values range from zero to unity. The sorbing power of paint films depends to a great extent on the paint film age and thickness. The values of paint films in this report range from 0.08 to 0.77. A small value is desirable from the decontamination viewpoint.

Finally, it should be mentioned that no real differences in behavior between the 5H and 20A paints were apparent.

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Recognition of the two characteristic periods has led to a modified approach to evaporation theory. This approach embodies the concept of a "standard dry line." The dry line is obtained by plotting t/r_p against t at various experimental conditions, where t is the evaporation time, and P_e is the percent of HD evaporated at that time. When evaporation is complete, i.e., P_e = 100%, the terminal points, for the different conditions, are found to form a straight line, i.e., the dry line. One consequence of the standard dry line concept is a method for determining or evaluating the sorbing power coefficient (x_p) of paint films. The sorbing power of paint films is the ability to absorb HD under a given set of experimental conditions. The K_{sp} values of paint films in these studies range from 0.08 to 0.77. A small value is desirable from the decontamination viewpoint.

There were no apparent differences in the behavior for the various types of paints used.

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